On the Magnetic Susceptibility and the Dipole Moment of Chlorosilane Having Phenyl Radical

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On the Magnetic Susceptibility and the Dipole Moment of Chlorosilane Having Phenyl Radical

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The magnetic susceptibilities of several organosilicon compounds were measured by the Gouy method. The observed values were compared with those calculated by Pascal's additive law. Only a chlorosilane having phenyl radical showed a considerably large difference between observed and calculated values. It was concluded that this discrepancy might result from the induced effect of chlorine atom on phenyl radical. Concerning this point, dipole moments of organosilicon compounds were measured and the induced effect of the dipole moment which one exert on one phenyl radical was given as 0.116 D. U.

I. INTRODUCTION

To discuss the induced effect of chlorine atom to phenyl radical in organochlorosilanes, measurements of magnetic susceptibilities and dipole moments were undertaken on thirteen organosilicon-compounds. Provided that all of the bonds in a molecule were covalent, the susceptiblities were calculated by use of Pascal's additive law. In the present case, the observed values of susceptiblity for most of the compounds studied were in agreement with those calculated by Pascal's law. Only one chlorosilane having phenyl radical showed a large discrepancy between observed and calculated susceptibilities. Speculating on this large discrepancy, it was concluded that this might result from the induced effect of chlorine atom on phenyl radical as mentioned below. In this connection, measurements of the dipole moment were carried out with the solution method.

II. MAGNETIC SUSCEPTIBILITY

As a preliminary test, the magnetic susceptibility was measured by the U-tube method (Quinck's method), but this method showed a considerable error due to a change of surface tension, and then the Gouy method[1] was used. In the latter case, a sample is inserted in a quartz tube, whose inner diameter and length are 2.5 mm and about 70 mm, respectively, and which is suspended from a balance by a quartz string. The one end of the tube is in a homogeneous field between the poles of a magnet, and the axis of the tube is held perpendicular to the magnetic field. The other end is in a region where the field is weak. The repulsive or attractive force by the field was measured by a balance.

The gram molecular susceptibility χ_M was calculated according to Pascal's

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law as follows :

$$\chi_M = \sum a\chi_A + \lambda$$

where a is the number of atoms in the molecule of susceptibility χ_A and λ is a constitutive constant depending on the nature of the bonds between the atoms. In this case, χ_A must be known. Although some atomic or ionic susceptibilities are given experimentally by Pascal[1], the other unknown susceptibilities must be calculated. We calculated the values of ions and atoms by the Slater-Angus method, where the calculated values of atoms (Si, O or C) slightly differ from the values given experimentally by Pascal, and then we revised the calculated values of ions so that the calculated value of its atom coincides with the experimental value (cf. * in Table 1). Results are given in Table 1. According to the Slater-

Table 1.

Calculated gram ionic (or atomic) susceptibility, unit—10^{-6}			
Si	20.0*	C	6.0*
Si^{+1}	13.9	C^{+1}	3.9
Si^{+2}	9.4	C^{+2}	2.5
Si^{+3}	5.0	C^{-1}	9.2
Si^{+4}	1.6	C^{-2}	13.9
O	4.6*	Cl	21.3
O^{-1}	6.6	Cl^{-1}	23.9
O^{-2}	8.5		

(* by Pascal)

Angus method, χ_A is given by

$$\chi_A = -\frac{Le^2}{6mc^2}\sum_N \overline{r^2}$$

where e is the electronic charge, m the electronic mass, c the velocity of light, L Avogadro's number, $\overline{r^2}$ the time average value of the square of the orbital radius of the Nth electron and the summation is taken over the N electrons in the atom. $\overline{r^2}$ was given as, by Slater

$$\overline{r^2} = \frac{(n')^2(n'+1/2)(n'+1)}{(Z-s)^2}$$

Table 2.

Compounds	Gram molecular susceptibility, unit-10^{-6}		
	Calc. ⓐ*	Obs. ⓑ**	ⓐ−ⓑ
$(C_2H_5)_3Si(OC_2H_5)$	132	124	8
$(CH_3)(C_2H_5)Si(OC_2H_5)_2$	124	116	8
$(CH_3)Si(OC_2H_5)_3$	129	116	13
$(CH_3)(C_6H_5)_2SiCl$	159	155	4
$(CH_3)(C_6H_5)SiCl_2$	127	101	26

* ⓐ, values calculated under the assumption of covalent bonds.
** ⓑ, values observed by the Gouy method.

where n' is the effective total quantum number, Z the nuclear charge, s the screening constant and $Z-s$ the effective molecular charge. Angus has shown that a slightly better agreement can be obtained by treating the s and p electrons as separate groups.

Observed and calculated magnetic susceptibilities are given in Table 2. (The values measured by the U-tube method are all omitted.) All but methyl-phenyl-dichlorosilane [$(C_6H_5)(CH_3)SiCl_2$] show small difference ⓐ−ⓑ of about -10×10^{-6} or less. It is found that the difference ⓐ−ⓑ does not particularly change, even when ionic bonds are taken into consideration instead of covalent bonds.

On the other hand, taking into consideration the validity of the values in Table 1 and the experimental error, it is difficult to discuss the type of bond only from such differences. Only phenyl-methyl-dichlorosilane, however, has the large difference ⓐ−ⓑ, which is fairly larger than the error mentioned above. Consequently, a considerable change in the bond of atoms should be expected. Speculating on this difference, we concluded as follows.

Table 3.

Bond between the carbon atoms	λ unit 10^{-6}	χ_A (including λ) for a carbon atom, unit 10^{-6}
>C−C<	0	−6.00
>C=C<	+ 5.5	−3.27
>C=C−C=C<	+10.6	−3.36
−C≡C−	+ 0.8	−5.61
	− 0.24	−6.24

λ : The constitutive constant depending on the nature of the bonds between the atoms.
χ_A : Gram atomic susceptibility.

Table 3 shows the susceptibilities of several C−C bonds, and the susceptibility of one carbon in a benzene ring is regarded as -6.24×10^{-6}, where the π electron circulates along the cyclic C−C bonds, and by this circulation its diamagnetic susceptibility increases by -0.24×10^{-6}. Now supposing that the electrons in benzen ring are drawn toward a silicon atom and thus such bonds as Fig. 1 are

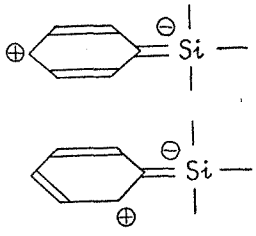

Fig. 1.

formed, such carbons may have the susceptibility as the double bond, and the diamagnetic susceptibility per carbon atom decreases by about -3×10^{-6}. Consequently, one phenyl radical shows the decrease of -18×10^{-6} which satisfies fairly well the above-mentioned difference. It seems to be reasonable that such an effect

is observed only for phenyl-methyl-dichlorosilane and not for diphenyl-monomethyl-chlorosiliane, considering the ratio of chlorine atom to phenyl radical. To discuss this speculation, from the other viewpoint, we investigated the dipole moment as mentioned below.

III. DIPOLE MOMENT

The dipole moment was measured by the dilute solution method[2] in which *n*-hexane was used as a non-polar solvent. Results are given in Table 4. Curran *et al.*[3] measured the dipole moments of some similar compounds to those examined here. Their data are given in the center column of Table 5. For discussing these moments, it was convenient to suppose the equivalent forms in

Table 4.

Compounds	MR_D	Temp. (°C)	P_∞	μ(D.U.)
$(CH_3)(C_6H_5)_2SiCl$	60.7	+20 −40	152.0 173.5	2.09 2.08
$(CH_3)(C_6H_5)SiCl_2$	44.9	+20	176.0	2.51

MR_D : Molar refraction for sodium D line
P_∞ : Molar polarization observed by dilute solution method
μ : Dipole moment

Table 5.

Compounds	Dipole moment (D.U.)	
	Obs. value△	Converted value for the supposed form (R−Si*−Cl)
$(C_2H_5)_3SiCl$	2.07	2.07
$(C_2H_5)_2SiCl_2$	2.39	2.07
$(C_2H_5)SiCl_3$	2.04	2.04
$(C_6H_5)_3SiCl$	2.14	2.14
$(C_6H_5)_2SiCl_2$	2.56	2.21
$(C_6H_5)SiCl_3$	2.41	2.41

(△ by Curran *et al.*)

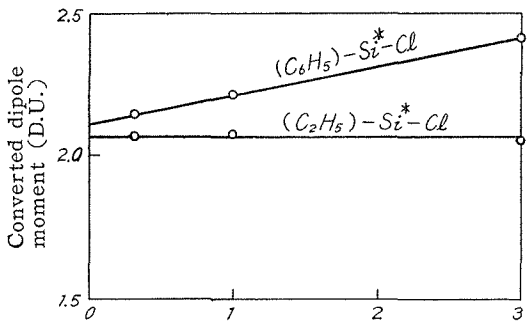

Fig. 2.

which R (organic radical), Si and Cl are on one line and in which the moments of these radicals are projected on the same axis. The dipole moments converted for the supposed form (R−Si*−Cl) are given in the right column of Table 5 and in Fig. 2 where the abscissa shows the number of Cl atom for one organic radical and the mark means the supposed form. In Fig. 2 it is found that the dipole moment of the chlorosilane having ethyl radical does not vary with the ratio of Cl to R, and on the contrary, the value of the one having phenyl radical increases in proportion to the ratio of Cl to phenyl radical.

We may conclude that these facts show the induced effect of Cl on phenyl radical. Based on this result, we calculated the induced effect which one chlorine influences on one pheny radical, and obtained a value of 0.116 D.U. Although our samples partially differ from the compounds in Table 5, provided that the dipole moment of a supposed straight form molecule $(CH_3)-Si^*-(C_6H_5)$ is zero, the above-mentioned induced effect is calculated as about 0.12 D.U. This coincidence of these two values is very satisfactory, and may justify the above speculation and suggests the dipole moments of trimethyl-phenyl-silane, etc. are nearly zero.

On the other hand, Robert *et al.*[4] and Freiser *et al.*[5] gave the values of 0.44 and 0.42 D.U., respectively, for the dipole moment of trimethyl-phenyl-silane. Based on our speculation, however, these both values might be miscalculated as a result of ignoring the error due to a computation of MR_D value which is larger in the case of a smaller dipole moment value. For instance, the two compounds of which the MR_D values are nearly equal and the dipole moments are considerably different, show respectively the following error in calculations of dipole moment,

$$\frac{\Delta\mu_2}{\mu_2}=\left(\frac{\mu_1}{\mu_2}\right)^2\cdot\frac{\Delta\mu_1}{\mu_1}$$

were μ_1 and μ_2 are dipole moments and μ_2 being very small.

Thus the uncertainty of the measurement of a small dipole moment value can be expected.

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